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CONFIGURATION OF ISOTACTIC POLYPROPYLENE

A THESIS

Presented to

the Faculty of the Graduate Division

By

Sam Alli

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Chemistry

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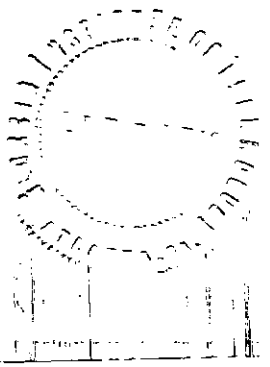

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CONFIGURATION OF ISOTACTIC POLYPROPYLENE

Approved:

Date approved by Chairman:

Jan. 30, 1961

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Notation Used in this Thesis

$\overline{R_o^2}$ = unperturbed mean-square end-to-end distance

$\overline{R^2}$ = mean-square end-to-end distance

α = expansion factor, equal to $(\overline{R^2}/\overline{R_o^2})^{\frac{1}{2}}$

α^* = viscosometric calibration constant

β = viscosometric calibration constant

ρ = density (g./cc.)

η = viscosity of solution

η_o = viscosity of solvent

η_{rel} = relative viscosity

η_{sp} = specific viscosity

$[\eta]$ = intrinsic viscosity

$[\eta]_\theta$ = intrinsic viscosity at theta temperature

k' = Huggins viscosity constant

k'' = Huggins viscosity constant

M = molecular weight

$\bar{M}_w$ = weight average molecular weight

$\bar{M}_n$ = number average molecular weight

$\bar{M}_v$ = viscosity average molecular weight

N = Avogadro's number

N_j = mole fraction

T_p = precipitation temperature

T_{el} = temperature of elution

Notation Used in this Thesis (continued)

T_m = melting point

Θ = theta temperature

W_x = integral weight distribution function

w = weight fraction

n_i = number of molecules of species i

c = concentration (g./dl.)

g. = grams

dl. = deciliter

μ_c = free energy per molecule in the bulk crystal

μ_1 = free energy per molecule in the bulk liquid

σ = interfacial free energy per unit area

n' = number of molecules in the sphere

r = radius of spherical crystalline body

v = volume per polymer molecule

$\bar{A}_2$ = average second virial coefficient

Φ = Flory's constant (2.4×10^{21})

XF(X) = permeation function of Kirkwood-Riseman

F(X) = Flory-Orofino function

n = degree of polymerization equal to $\bar{M}/M_o$

K = constant in the equation $[\eta] = KM^a$

a = constant in the equation $[\eta] = KM^a$

V_e = effective volume

R_e = effective radius

ϕ = rotation angle

Notation Used in this Thesis

$V(\phi)$ = hindrance potential

l = bond length

τ = turbidity

H = light scattering constant

SUMMARY

1. An elution column chromatographic technique was used to fractionate a sample of isotactic polypropylene. To elute the fraction from the column, a binary mixture of solvent and non-solvent in conjunction with a variation in column temperature were used. Several fractions were characterized by means of viscosity measurements. The results indicate that reasonable fractionation occurred in the low molecular weight range.

2. The initial results of a study of the phase diagram of the system naphthalene-polypropylene suggested that naphthalene was a "theta" solvent but refinements in the experimental technique failed to confirm this expectation.

3. Intrinsic viscosity measurements were performed on dilute solutions of polypropylene to determine the configuration of the molecule as a function of molecular weight and temperature in two solvents, diphenyl ether and α-chloronaphthalene. From the results of the influence of temperature and solvent on the intrinsic viscosity of polypropylene, it is concluded that this polymer is similar in its configurational properties to other vinyl type polymers. To confirm this conclusion, the unperturbed

dimension of a polypropylene molecule was estimated with the aid of a modified expression of Orofino and Flory using entirely the data from other workers (Kinsinger and Parrini, Sebastiano and Messina). It was found that in the solvent α-chloronaphthalene the value of $\overline{R_0^2}/M$ for a polypropylene molecule is not significantly different from that of other vinyl polymers. For example, in comparison with isotactic polystyrene and polyisobutylene the value of the mean-square end-to-end distance per repeating unit, $\overline{R_0^2}/n$ (equal to $\overline{R_0^2}/\frac{M}{M_0}$) was calculated to be 58 x 10^{-16} cm^2 (at 30°C) and 32 x 10^{-16} cm^2 (at 24°C), respectively, while the value for polypropylene is 33 x 10^{-16} cm^2 (at 30°C). Furthermore, the value of the temperature coefficient of $\overline{R_0^2}/M$ of -.35 x 10^{-18} $cm^2/g./mole/deg.$ for isotactic polypropylene compares favorably with the value for atactic polystyrene, -.65 x 10^{-18} $cm^2/g./mole/deg.$ Values of the expansion factor, α (by which the root-mean-square end-to-end distance is expanded due to net repulsive forces between widely separated segments within a chain), were calculated in the present investigation in conjunction with the Flory-Orofino expression, and using the values of the intrinsic viscosity measured in α-chloronaphthalene. These expansion factors were found to increase with temperature for a given molecular weight as expected. However, both this work and that of the above mentioned workers show α to be essentially constant as M varies at constant temperature, whereas

theory predicts an increase. No explanation is offered for this anomaly.

CHAPTER I

INTRODUCTION

The two quantities which best characterize a linear polymer molecule are its molecular weight and its average molecular configuration in dilute solution. The concept of the molecular weight of a polymer requires careful definition in order to avoid ambiguity, since an actual given sample is composed of polymer molecules of many different molecular weights. This ambiguity can be avoided by referring to an average molecular weight (for example, the "number average" molecular weight is defined as the total weight of a sample of the polymer divided by the total number of moles of molecules which it contains, or

$$\overline{M}_N = \sum N_i M_i = \frac{\sum n_i M}{\sum n_i} ,$$

where N_i is the mole fraction defined by

$$N_i = \frac{n_i}{\sum n_i}$$

and n_i is the number of molecules of species i). The average molecular configuration can be conveniently expressed by the root-mean-square end-to-end distance $(\overline{R^2})^{\frac{1}{2}}$. In the following paragraphs this concept will be developed.

A convenient representation of a hydrocarbon polymer molecule on paper is a planar zig-zag sequence of the carbon atoms in the main chain (Figure 1):

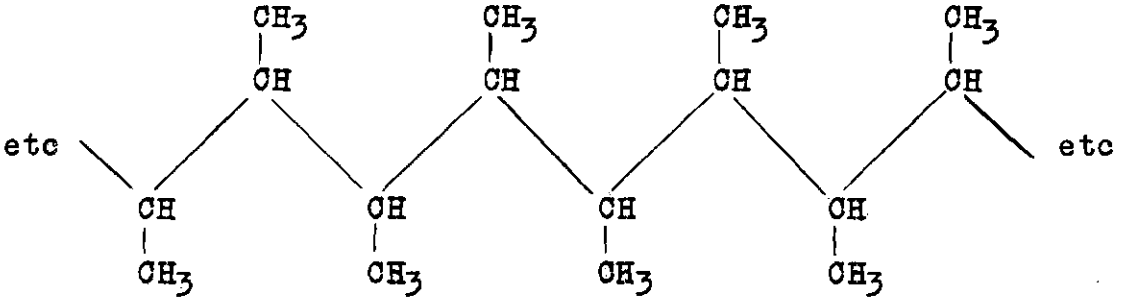

Figure 1. Extended Polypropylene Molecule

This, however, represents only one configuration out of the great number which are possible, in view of the freedom of rotation about the chain backbone bonds. Hence, it is meaningful to speak only of the <u>average</u> configuration of a molecule, since thermal energy is ordinarily sufficient to allow a given molecule to successively assume all of its possible configurations by appropriate internal rotations.

Physical properties which depend on the configuration of the polymer molecules can be expressed as functions of an average dimension (1). A quantity which can be used to partly characterize the configuration of a molecule is the distance R from one end to the other. The simplest non-zero average of this distance is the root-mean-square end-to-end

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(1) P. J. Flory, <u>Principles of Polymer Chemistry</u>, Cornell University Press, Ithaca, New York, 1953, Chapter X.

distance $(\overline{R^2})^{\frac{1}{2}}$ ($\overline{R}$ itself is zero). This root-mean-square end-to-end distance of the chain enters directly into theoretical treatments of the viscosity of dilute polymer solutions (2).

Among the factors upon which the configuration of a polymer molecule depends is that of interactions with the solvent. In a "good" solvent, where the interactions between polymer segments and solvent molecules are energetically favored relative to those of segment-segment and solvent-solvent, the polymer molecule will tend to be found in configurations for which the end-to-end distance is large, since the number of polymer-solvent contacts is thereby increased. In a "poor" solvent, on the other hand, where the segment-solvent interactions are less favorable, the polymer molecule tends to assume configurations for which the end-to-end distance is smaller, since the number of segment-solvent interactions is thereby decreased. Hence, $\overline{R^2}$ is larger for a given molecular weight and temperature, the better the solvent.

Another factor which affects molecular dimensions is that of hindrance to rotation about the chain backbone bonds of the polymer molecule. The energy of a given configuration is a function of a set of angles ϕ_i (the position taken up

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(2) J. G. Kirkwood and J. Riseman, J. Chem. Phys., 16, 565 (1948).

by atom (i + 1) may be characterized by the angle ϕ_{i+1} made by the plane containing the i - 2, i - 1 and i atoms and the plane containing i - 1, i, and i + 1). Different values of ϕ will correspond to different repulsive forces between atoms bonded to adjacent chain atoms. Thus, even in the simplest hydrocarbon polymer, polymethylene, repulsive forces between hydrogen atoms on adjacent carbon atoms leads to hindered rotation about the C - C bond. A hindrance potential $V(\phi)$ is thus associated with the rotation angle ϕ. This function is symmetrical about the position $\phi = 0$ as measured from the trans orientation in the case of polymethylene. If large substituents such as phenyl groups are introduced into the carbon chain (e.g. in polystyrene) the hindrance is greatly increased and also becomes unsymmetrical. For the simplest case of a symmetrical hindering potential (see Figure 2), as in the case of polymethylene, it has been shown that the mean-square distance between chain ends (3, 4, 5) is

$$\overline{R^2} = nl^2\left(\frac{1-\cos\theta}{1+\cos\theta}\right)\left(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}}\right)$$

where n is the number of bonds of identical length l joined at valence angles θ. The quantity $\overline{\cos\phi}$ is the average value

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(3) W. J. Taylor, ibid., 16, 257 (1948).

(4) H. Benoit, J. chim. phys., 44, 18 (1947).

(5) H. Kuhn, J. Chem. Phys., 17, 303 (1947).

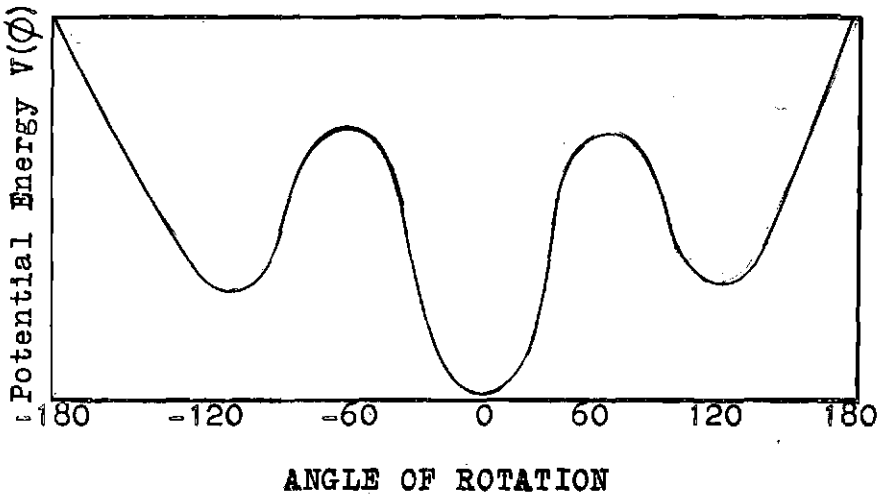

Figure 2. Symmetrical Potential Energy Diagram

of $\cos\phi$,

$$\overline{\cos\phi} = \int_0^{2\pi} (\cos\phi)\, e^{-\frac{V(\phi)}{kT}}\, d\phi$$

If the rotation is unrestricted, $V(\phi)$ is constant and $\overline{\cos\phi} = 0$. Whereas repulsive forces between atoms on adjacent carbon atoms causes $V(\phi)$ and thus tend to vary with ϕ, usually in such manner as to increase the average dimension for any real polymer molecule.

In any event temperature will affect the value of $\overline{R^2}$, rotational angles corresponding to higher values of $V(\phi)$ being more probable at higher temperatures. The situation in practice is even further complicated by the circumstance that the rotations about the various bonds in the chain cannot really be independent, as has been implicitly assumed in the preceeding remarks.

In a sufficiently poor solvent where the interaction energy with the polymer is positive (unfavorable) the tendency of the molecule to contract may exactly compensate the tendency of the molecule to expand due to "volume exclusion" effects (6, 7). By this expression is meant that the net repulsive forces between segments distantly connected in the chain prevent the effective overlap in space implicitly allowed by "random flight" statistical considerations. The polymer molecule under this unique condition then obeys random flight statistics (8, 9), its dimensions being determined solely by molecular weight, bond lengths and angles, and temperature. This condition occurs at a definite temperature (the so-called theta temperature) for a given polymer-solvent system. Hence, for a given polymer-solvent system measurements made at this temperature reveal the characteristics of the polymer molecules themselves, "unperturbed" in the sense of having any deviations from random flight statistics.

A notable property of polymer molecules is the ability they have to greatly increase the viscosity of a liquid when they dissolve in it. This is due to the rather large volume

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(6) W. R. Krigbaum, ibid., 23, 2113 (1955).

(7) H. M. James, ibid., 21, 1628 (1953).

(8) P. J. Flory, ibid., 15, 843 (1947).

(9) P. J. Flory and T. G. Fox, Jr., J. Am. Chem. Soc., 73, 1904 (1951).

effectively pervaded by each of the randomly coiled long chain molecules. The higher the molecular weight, the greater is the increase in viscosity for a given concentration. Hence, viscosity measurements afford a method of measuring molecular weight. It was Staudinger (10, 11) in 1930 who first extensively used viscosity measurements of dilute polymer solutions as a means of characterizing polymers.

At this point it will be helpful to define certain quantities that are required to discuss solution viscosities. The viscosity, η, is a measure of resistance to flow and is defined by Newton's equation relating shearing stress (f) to rate of shear ($\frac{ds}{dt}$) as follows:

$$f = \eta \frac{ds}{dt}$$

Thus, the dynamic viscosity, η, of a liquid is the tangential force on unit area of either of two parallel planes at unit distance apart when the space between these planes is filled with the liquid being studied and one of the planes moves with unit velocity in its own plane relative to the other. The unit of the dynamic viscosity in the c.g.s. system is the "poise" (one dyne second cm^{-2}). If the dynamic viscosity is divided by the density one obtains the kinematic viscosity (ν), the c.g.s. unit of which is the "stoke".

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(10) H. Staudinger and W. Hever, Ber., 63, 222 (1930).

(11) H. Staudinger and R. Nodzu, ibid., 63, 721 (1930).

The viscosities of polymer solutions are commonly measured in capillary viscometers (12). The viscosity is given under the simplest conditions by the formula of Poiseuille:

$$\eta = \frac{\pi a^4 P}{8l(\frac{dV}{dT})}$$

where a is the radius of the capillary, l is the length of the capillary, P is the driving pressure and $(\frac{dV}{dT})$ is the rate of efflux (13). The measurement consists simply of the time of flow t of a given volume of solution through the capillary. In practice, so-called "kinetic energy" and "end effects", corrections both unaccounted for by Poiseuille's formula, must be reckoned with. In accurate work these corrections (14) are usually taken into account by employing the equation:

$$\eta = \alpha^* \rho (t - \frac{\beta}{\alpha t})$$

where ρ is the density of the liquid, and α^* and β are constants for a given capillary instrument and volume of liquid. They are obtained by calibration with water, whose

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(12) P. W. Allen (ed.) Techniques of Polymer Characterization, Butterworth Scientific Publication, London, 1959, pp. 184-194.

(13) F. R. Eirich (ed.) Rheology Theory and Application, Vol. 3, Academic Press Inc., New York, N. Y., 1960, pp. 127-129.

(14) G. Barr, A Monograph of Viscosity, Oxford University Press, London, 1931, pp. 125-127.

viscosity as a function of temperature is well known (15). The second term accounts for the "kinetic-energy" effects.

The relative viscosity of a polymer solution is defined as the quotient of the viscosity of the solution, η, and the viscosity of the solvent, η_o:

$$\eta_{rel} = \frac{\eta}{\eta_o}$$

The fractional increase of the solution viscosity upon addition of polymer is called the specific viscosity, η_{sp}:

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \eta_{rel} - 1$$

The value of η_{sp}/c is then, a measure of the fractional increase of the viscosity of a solution of unit concentration. The value of η_{sp}/c at infinite dilution is called the intrinsic viscosity, $[\eta]$, :

$$[\eta] = \lim_{c \to o} \left(\frac{\eta_{sp}}{c}\right)$$

The intrinsic viscosity (usually expressed in units of deciliters per gram) is then, a measure of the contribution of one gram of isolated polymer molecules to the fractional increase in viscosity of a deciliter of solution. It is this quantity which is most fundamentally related to the size and shape of polymer molecules.

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(15) American Society for Testing Material Standards, Part 5, "Kinematic Viscosity", American Society for Testing Materials, Philadelphia, Pa., 1949, pp. 899-909.

A theoretical treatment of hydrodynamic properties of polymer solutions has been given by Kirkwood and Riseman (2). This treatment assumes that the polymer chains follow random flight statistics (16, 17, 18) (i.e. that $\overline{R^2} \sim M$). There results from this theory the relationship

$$[\eta] = [XF(X)] \frac{(\overline{R^2})^{3/2}}{M} ,$$

where XF(X) is a "permeation function" which increases with molecular weight to an upper asymptotic limit at a value of M not predictable by theory. For small impermeable spheres Einstein has shown that the intrinsic viscosity is proportional to the volume (v) of a sphere divided by the molecular weight (19). For "spheres" which are actually extended coils plus imbibed solvent, an effective volume (V_e) can be defined so that

$$[\eta] \sim \frac{V_e}{M}$$

The volume of a sphere is proportional to the cube of the radius; therefore

$$[\eta] \sim \frac{Re^3}{M}$$

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(16) Lord Rayleigh, Phil. Mag., 6, 37, 321 (1919).

(17) S. Chandrasekhar, Rev. Mod. Phys., 15, 3 (1943).

(18) P. Debye, J. Chem. Phys., 14, 636 (1946).

(19) F. R. Eirich (ed.) Rheology Theory and Application, Vol. 1, Academic Press Inc., New York, N. Y., 1956, Chapter 14.

Thus the effect of the permeation function XF(X) is that R_e increases more rapidly with molecular weight than does $(\overline{R^2})^{\frac{1}{2}}$, until the molecular weight is high enough so that the asymptotic limit is reached. Flory (5, 9) in his extension of the above treatment has proposed: (a) that the permeation function is at its asymptotic limit for flexible polymers over the entire molecular weight range of interest, and hence that $R_e \sim (\overline{R^2})^{\frac{1}{2}}$, (b) that $(\overline{R^2})^{\frac{1}{2}}$ is in general expanded over the corresponding dimension for the unperturbed configuration by a factor α which increases with M due to "volume exclusion" effects (cf. above).

The proposed proportionality between the hydrodynamic radius and $(\overline{R^2})^{\frac{1}{2}}$ provides a means of characterizing the polymer. Now

$$[\eta] \sim \frac{R_e^3}{M}$$

$$R_e \sim (\overline{R^2})^{\frac{1}{2}}$$

Therefore,

$$[\eta] = \Phi \frac{(\overline{R^2})^{3/2}}{M} = \Phi \left(\frac{(\overline{R_0^2})}{M}\right)^{3/2} M^{\frac{1}{2}} \alpha^3 \qquad (1)$$

where Φ is a constant, independent of temperature, solvent and of the molecular weight of the polymer. The quantity α is the factor by which $(\overline{R^2})^{\frac{1}{2}}$ differs from the value it would have at the theta temperature. Values of α greater than unity correspond to net repulsive forces between distantly

connected segments of the chain, and values less than unity correspond to net attractive forces (i.e. when $\alpha = 1$ then these "volume exclusion" effects vanish, and the polymer molecules are said to be unperturbed). Designating the intrinsic viscosity under "theta" conditions as $[\eta]_\theta$, we see from equation (1) that α can be calculated from a measurement of $[\eta]$ from the relationship

$$\alpha^3 = \frac{[\eta]}{[\eta]_\theta} \qquad (2)$$

Most information on the dimensions of crystalline polymers is obtained in good solvents in which the molecular dimensions are expanded due to such long range interferences. Solvents which are theromodynamically "poorer" do not dissolve the polymer. Thus $[\eta]_\theta$ cannot be measured directly for such polymers. Orofino and Flory (20) present a relationship between the second virial coefficient and intrinsic viscosity which makes it possible to estimate dimensions of polymer molecules. Their result is

$$\frac{27\,\Phi\, A_2 M}{2^{5/2}\, N\pi[\eta]} = \ln\left[1 + \frac{\pi^{\frac{1}{2}}}{2}(\alpha^2 - 1)\right]$$

When appropriate modification is made to account for polydispersity (21a), one obtains (21b)

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(20) T. A. Orofino and P. J. Flory, J. Chem. Phys., 26, 1067 (1957).

(21) P. J. Flory and W. R. Krigbaum, ibid., 18, 1086 (1950), J. Voeks, J. Polymer Sci., 36, 333 (1959).

$$2.76 \times 10^{-24} \bar{A}_2 \bar{M}_w \Phi [\eta]^{-1} = \overline{F(X)\ (\alpha^2-1)} \qquad (3)$$

where $\bar{A}_2$ is the light-scattering second virial coefficient (defined as the initial slope of Hc/τ vs c plot where c is the concentration, τ the turbidity and H is a constant for a particular polymer-solvent), $\bar{M}_w$ is the weight average molecular weight, Φ is a constant, N is Avogadro's number and where the function F(X) (not to be confused with XF(X) of the Kirkwood-Riseman theory) is given by (21a)

$$F(X) = 2 - \frac{X}{2!2^{3/2}} + \frac{X^2}{3!3^{3/2}} - \ldots. \text{ and } X = 2(\alpha^2 - 1)$$

If this calculation is carried out at two temperatures one can obtain $[\eta]_\theta$ at these two temperatures (using the equation (2) ($[\eta]_\theta = \frac{[\eta]}{\alpha^3}$). Once $[\eta]_\theta$ is known at two temperatures one can evaluate $(\overline{R_0^2}/M)$ as a function of temperature (using the equation (1) $[\eta]_\theta = \Phi(\overline{R_0^2}/M)^{3/2} M^{\frac{1}{2}}$). Thus, this calculation requires $[\eta]$, A_2 and α to be known as functions of temperature in good solvents.

When a propylene molecule ($CH_3CH{=}CH_2$) is polymerized by an addition type polymerization process, a single propylene monomer molecule is first activated; this then attacks another monomer to yield another activated species. The successive addition of monomers then continues until some chain-terminating mechanism occurs. The configuration of the groups around a given asymmetric carbon atom (i.e., d or l) depends

upon the orientation of a monomer molecule as it adds to the growing chain. If monomer molecules add in such a way that an ordered sequence on the asymmetric carbon atom is obtained (e.g. ddd..... or dldldl..... or lll.....) the resultant polymer is called a stereospecific polymer. If the d and l configurations of the asymmetric carbons occur randomly, the polymer is called an atactic polymer. A polypropylene molecule in which the asymmetric carbon atoms have the same stereochemical configuration (all d or l) is called isotactic. This type of polymer is ordinarily crystalline whereas atactic polypropylene (no order in d, l of the asymmetric carbon atoms along the chain) is amorphous.

The solubility characteristics and bulk properties of isotactic and atactic polymers are significantly different. This question has been discussed in several recent papers (22, 23, 24, 25). It was found that for isotactic polystyrene (26) in the unperturbed state the value of $\overline{R_o^2}/M$ at room temperature is ca. 10 per cent larger than the corresponding value for atactic polystyrene.

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(22) F. Danusso and G. Moraglio, Makromol. Chem., 20, 37, (1956).

(23) F. Danusso and G. Moraglio, J. Polymer Sci., 24, 161 (1957).

(24) F. W. Peaker, ibid., 22, 25 (1956).

(25) J. Ang, ibid., 25, 126 (1957).

(26) W. R. Krigbaum, D. K. Carpenter, and S. Newman, J. Phy. Chem., 62, 1586 (1958).

If the potential energy hindering rotation about an angle ϕ, $V(\phi)$, of one of the chain bonds is considered, one might expect intuitively a somewhat larger unperturbed dimension for the isotactic polymer over the atactic. This potential function, $V(\phi)$, is an unsymmetrical function of the angle ϕ for repeating units of the type $-CH_2-CHR-$ (see Figure 2.). This means that a rotation in one of the directions is energetically preferred over a corresponding rotation in the opposite direction. One might expect that steric interferences between atoms directly attached to two successive atoms in a chain (assuming no interferences between other atoms during the rotation) would be greater for the isotactic polymer than for the atactic polymer. This would result in a larger root-mean-square end-to-end distance for isotactic polypropylene.

In order to study the configuration and its temperature dependence, measurements are reported here of the intrinsic

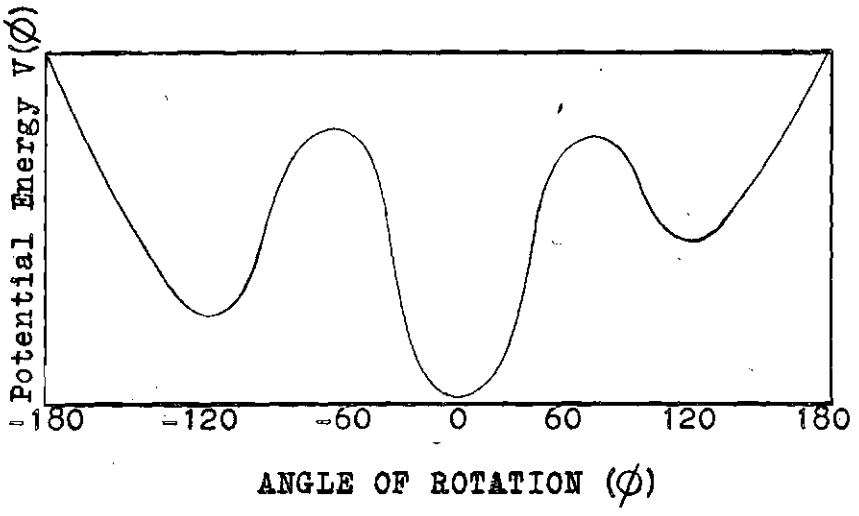

Figure 3. Unsymmetrical Potential Energy Diagram

viscosity of isotactic polypropylene as a function of temperature in diphenyl ether (a theta solvent) and α-chloronaphthalene (a good solvent). The samples used were obtained by a column fractionation procedure. The phase diagram of the system naphthalene-polypropylene was examined in conjunction with trying to obtain a second theta solvent. Further work, on determining the configuration of atactic polypropylene would be helpful in disclosing the difference in configuration between isotactic and atactic polypropylene.

CHAPTER II

EXPERIMENTAL

A. Description of Materials

Polypropylene.--The samples of polypropylene used in these experiments were manufactured by the Hercules Powder Company. The isotactic (crystalline) polypropylene pellets were hard, white and slightly opaque. The polypropylene was probably cut into small pellets after being extruded. The intrinsic viscosity of the unfractionated polymer in decalin at 135° C was found to be 2.69 dl/g. which corresponds to a molecular weight of 306,000 using the following relationship (27)

$$\text{Log } [\eta] = -3.959 + .80 \log \bar{M}_v$$

Decalin.--The decalin used for viscosity determinations was obtained from two sources, Eastman Organic Chemicals and Matheson, Coleman and Bell. Purification of this solvent was carried out by washing successively with sulfuric acid and water. The decalin was dried using sodium. It was then distilled through a fractionating column, a portion boiling at 189.0°-193.4° C being collected. The distilled decalin was stored over sodium wire.

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(27) J. B. Kinsinger and R. E. Hughes, J. Phys. Chem., 63, 2002 (1959).

α-Chloronaphthalene.--Eastman's white label grade α-chloronaphthalene was vacuum distilled at 7 mm. and a portion collected boiling between 107°-109° C. The refractive index found at 21.6° C was 1.6300 (Literature value $n_D^{21.6}$ = 1.63184 (28).

Diphenyl Ether.--The diphenyl ether obtained from Matheson, Coleman and Bell was distilled at 0.1 mm. in a 24-inch packed column, a 500 cc. portion boiling at 110-112° C being collected.

Diethylene Glycol Diethylether.--The diethylene glycol diethylether (186°-188° C) and decalin used in the fractionation procedure were obtained from Eastman Organic Chemicals and Matheson, Coleman and Bell respectively, and were distilled without prior purification.

Stabilizers.--Stabilizers used for the polymer solutions were Ionol (2,6-di-tert.-butyl-p-cresol) obtained from Eastman Organic Chemicals, used without further purification, and stannous sterate, obtained through the compliments of the Monsanto Company, also used as received. Both were dried in a vacuum oven overnight at 50° C (±10°) before using.

Naphthalene.--Naphthalene (source unknown) was purified by distilling. A fraction boiling at 213°-215° C was collected.

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(28) E. H. Huntress, Organic Chlorine Compounds, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 914.

Xylene.--Technical xylene, used for cleaning glassware was obtained from Matheson, Coleman and Bell and distilled at 135°-140° C.

B. Fractionation of the Polymer

The elution column chromatography technique was chosen for this purpose. This technique was first used by Desreux and Spiegels (29) to fractionate polyethylene. Elution fractionation was also carried out on linear polyethylene by Francis, Cooke and Elliot (30). Column fractionation techniques have been carried out using various types of supports such as sand, glass beads, and charcoal (31, 32, 33). P. M. Henry (34) used celite as the support for polyethylene in his elution fractionation technique.

After the polymer is deposited on the support polymer fractions are eluted from the column. Several types of

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(29) V. Desreux and M. C. Spiegels, Bull. Soc. chim. Belges, 59, 476 (1950).

(30) P. S. Francis, R. C. Cooke, and J. H. Elliot, J. Polymer Sci., 31, 453 (1958).

(31) C. A. Baker and R. J. Williams, J. Chem. Soc., 2352 (1956).

(32) W. R. Krigbaum and J. E. Kurz, J. Polymer Sci., 61, 275 (1959).

(33) K. Lawrence Distillers Company Ltd., Unpublished work, referred to in Allen (ed.) op. cit., p. 43.

(34) P. M. Henry, J. Polymer Sci., 16, 3 (1959).

variations are possible in removing the polymer from the column. The elution may be a process which is continuous or stepwise. The former was chosen in this procedure. Also, the elution of the polymer from the column may be carried out by using a single solvent and varying the temperature or by using a binary mixture of non-solvent and solvent that contains gradually increasing amounts of solvent at a constant temperature (35, 36), or by a combination of the two methods (31, 32). A binary mixture was used in the present work. The non-solvent used, diethylene glycol diethylether, was gradually diluted with solvent, decalin, so that the composition of the eluent changed from pure diethylene glycol diethylether to a mixture of decalin and diethylene glycol diethylether which is progressively richer in decalin. The rate of flow of eluent mixture through the column was in the vicinity of 50-75 ml. per hour.

The fractionation apparatus (Figure 4) used consisted of a column 195.6 cm high, fabricated from 75 mm. o.d. pyrex tubing for the outer jacket and 51 mm. o.d. tubing for the inner column. The jacketed column permits the maintenance of the support at a constant temperature by refluxing the liquid in pot C. Heat loss was minimized (as can be seen in the photograph, Figure 5) by wrapping the column with asbestos

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(35) V. Desreux, op. cit., 57, 416 (1948).

(36) V. Desreux, Rec. Trav. chim. Pays-Bas, 68, 789 (1949).

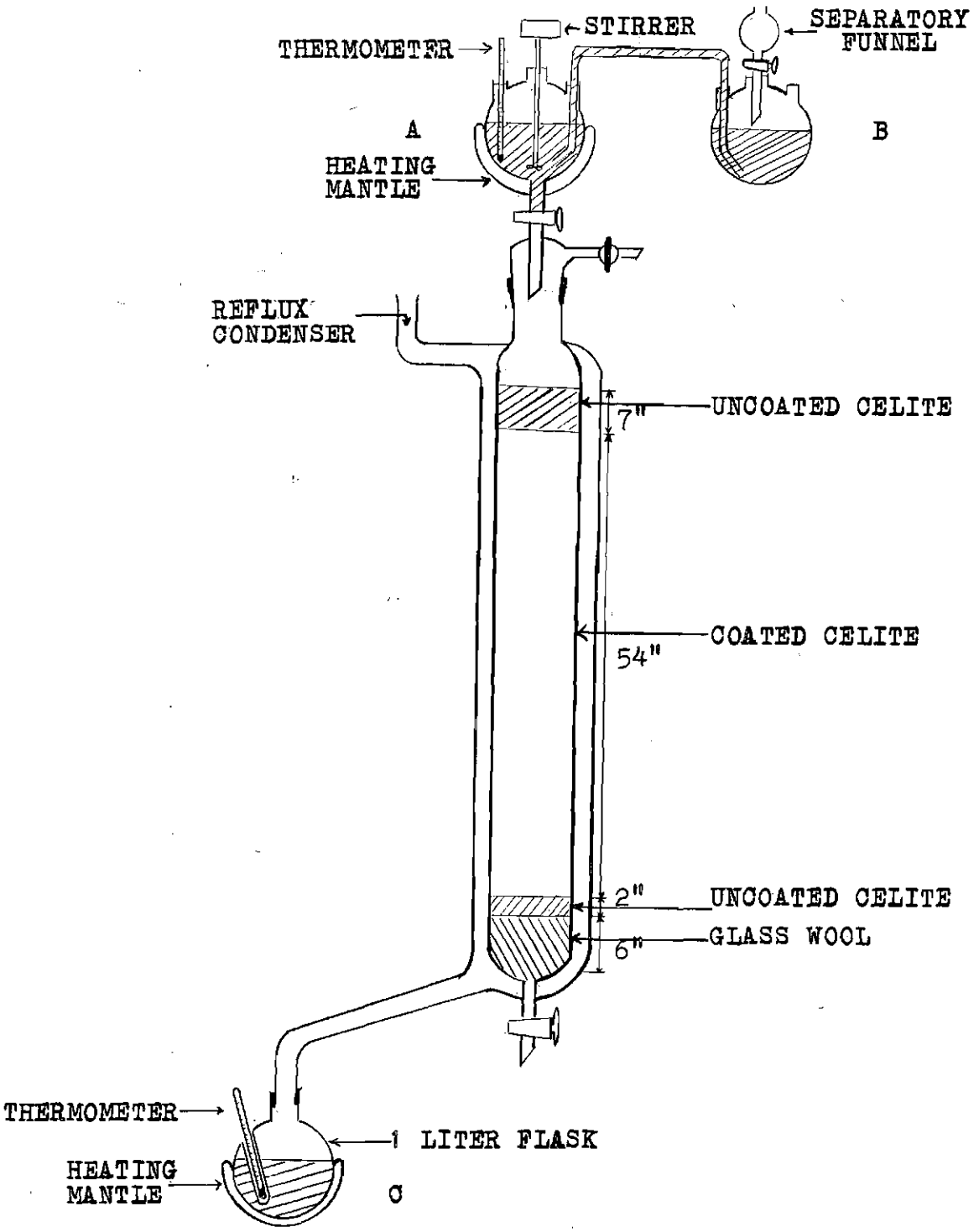

Figure 4. Fractionation Apparatus

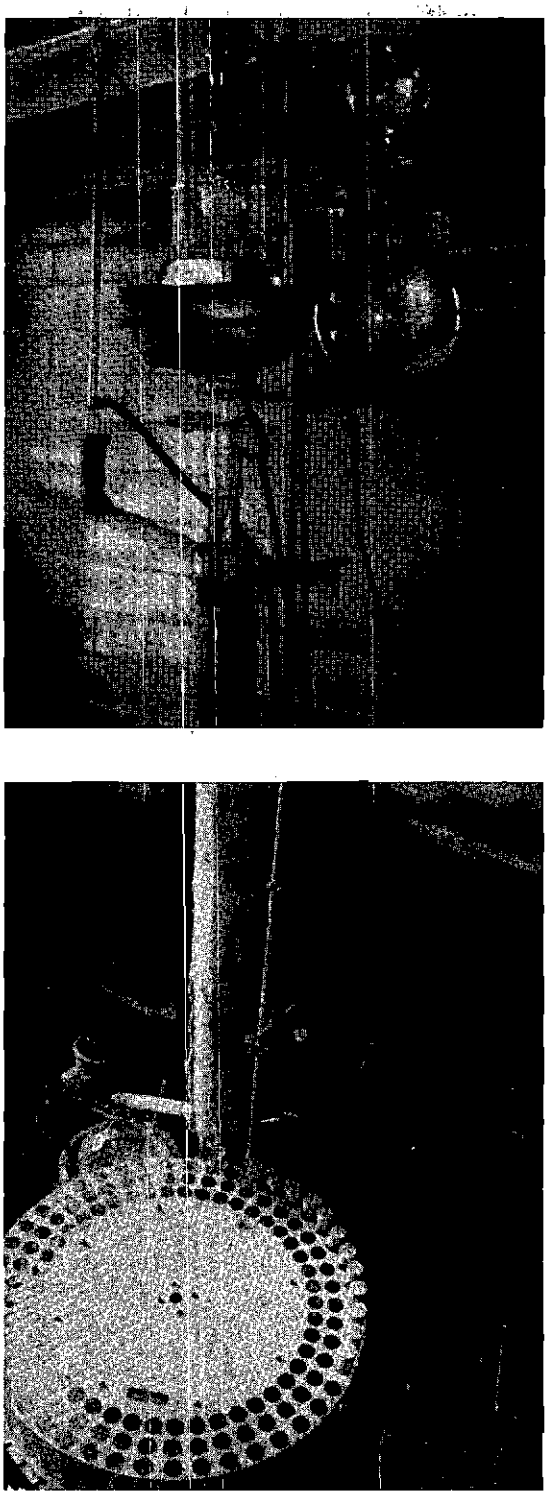

Figure 5. Photograph of Fractionation Apparatus.

coated with water glass. The lower part of the column was filled with six inches of glass wool. Above this were placed two inches of uncoated celite. The column was then filled with about fifty-three inches of polymer coated celite. Seven inches of uncoated celite were then added at the top so that the eluent entering from the reservoir would be at the same temperature as the polymer when it reached it. The eluent was stirred and preheated in the flask A to a temperature near that of the column. This is necessary in order to prevent as much as possible reversals in the order of molecular weights (37) extracted from the column. The solvent in flask B was initially a 1:1 mixture of decalin and diethylene glycol diethylether and, as described above, increased in decalin concentration as the fractionation proceeded.

In the fractionation performed, into a 5 liter three neck r.b. flask were placed 660 g. of celite, 0.30 g. Ionol (2,6,-di-tert.-butyl-p-cresol,a stabilizer for polypropylene) and 3250 ml of decalin. This slurry was heated by a heating mantle and stirred with a Tru-bore stirrer and Teflon paddle. When the temperature of 145° C was attained 24.9 g. of polypropylene were added. The temperature was then held constant for one hour with vigorous stirring. After this time the polymer had dissolved and the temperature of the slurry was

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(37) A. S. Kenyon and I. O. Salyer, J. Polymer Sci., 63, 427 (1960).

then slowly decreased by controlling the heating mantle on the r.b. flask. The rate of cooling for the slurry was 0.17 C ^{o}/min. (The object of this slow cooling process was to have the higher molecular weight species precipitate first on the celite particles, since they are more insoluble. As the temperature decreased, successively lower molecular weight species would then deposit in successive layers, each coating over that of the next higher molecular weight species. Upon subsequent elution, the lower molecular weight species would thus be the first to be removed.) After cooling the slurry down to room temperature it was filtered thru a coarse ground glass frit funnel. Most of the decalin was removed by washing with acetone. (Since acetone is a non-solvent the polymer that was not tightly coated onto the celite support was precipitated from solution at this point. This precipitate was filtered by medium porosity filter paper, dried in a vacuum oven and weighed. The amount of polymer uncoated on the column was thus found to be 1.16 g.) The celite had a strong odor of acetone so it was placed in a vacuum oven overnight.

A slurry was made with the polymer-coated celite and the non-solvent diethylene glycol diethylether. This slurry was then put into the column which already contained some diethylene glycol diethylether. Preliminary experiments showed that the column could be best packed without the inclusion of air bubbles by heating the slurry and leaving the

column filled with some non-solvent before the addition is made.

The rate of elution of polymer from the column was controlled by means of the stopcocks at the bottom and the top of the column. The polymer solutions were collected at the bottom of the column in 80 ml. test tubes which contained approximately 15 ml. of acetone. The polymer precipitated in the test tubes. (The test tubes were held in an automatic fraction collector working on a "time" basis.) The test tubes were then placed in a refrigerator overnight to ensure completeness of precipitation. Then the polymer suspensions were added to equal volumes of acetone and shaken vigorously. These suspensions were filtered on previously weighed filter papers. The polymer fractions were then washed with acetone. The filter papers with polymer were placed in petri dishes and left in a vacuum oven at 60° C overnight. The dried polymer fractions were again weighed to determine the total amount recovered. The amount of the original polymer coated on the column recovered by the fractionation as carried out was 90 per cent. The foregoing treatment of the polymer gave fractions in a white powdery form.

C. Phase Equilibria

Preliminary work on the polypropylene-naphthalene system was carried out in six inch pyrex test tubes con-

taining a stirrer mounted thru a stopper containing a glass cylinder shaft. The close fitting of the stirrer and cylinder was used to minimize evaporation of the solvent. The apparatus was immersed in an oil bath.

Determination of the precipitation temperature, T_p, was carried out by visual observation. Other workers (38) have found that precipitation measurements using photoelectric turbidimeters afford no increase in sensitivity.

The polypropylene sample and the solvent were weighed into the apparatus and stirred above the precipitation temperature until the polymer completely dissolved. Solutions of various concentrations of polypropylene and napthalene (plus stabilizer) were prepared ranging from 1 per cent to 25 per cent by weight of polymer. Higher concentrations of polymer dissolved with difficulty. Therefore, higher temperatures (135° to 145° C) were used to dissolve these samples. After the polymer dissolved the oil bath temperature was then decreased to effect precipitation of the polymer. A broken thermometer was placed directly behind the solution test tubes in such a way that the scale could be read. The temperature, T_p, was noted as the temperature at which blurring of the thermometer scale occurred.

The initial results for this system were quite interesting since they suggested that liquid - liquid phase

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(38) A. R. Shultz and P. J. Flory, J. Amer. Chem. Soc., 74, 4760 (1952).

separation occurred over the concentration range studied. If this were so, then from the phase diagram for different molecular weights the critical consolute temperatures could be determined, and from these the theta temperature for polypropylene in naphthalene could be determined by extrapolation to infinite molecular weight (39). Viscosity measurements in the two theta solvents diphenyl ether and naphthalene would then have given information about the configuration of polypropylene chains at the two temperatures corresponding to theta conditions in these two solvents. However, reproducible results were not obtained when carried out with new samples.

In view of the foregoing, a new arrangement was used in which solvent evaporation was prevented from occurring and oxidative degradation was minimized.

Test tubes, 5 mm. o.d. and approximately 15 cm. long, were used for the polymer solutions of concentrations ranging from 1 to 11 per cent by weight of the polymer. The reason higher concentrations were not used was the extreme difficulty in dissolving the polymer by shaking with the small volume of solvent used (approximately 1 cc.). After placing the weighed samples in the test tubes, the test tubes were evacuated and then sealed under a nitrogen atmosphere.

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(39) H. Tompa, Polymer Solutions, Butterworth Scientific Publication, London, 1956, pp. 207-211.

The seal was made at least one inch from the bottom, while the bottom portion of the test tube containing the mixture was immersed in dry ice to prevent evaporation of the naphthalene. These were then placed in a rack suspended in a thermostat which contained a thermometer scale mounted directly behind the tubes so that T_p could be observed (when the scale blurred). This method was convenient since it allowed the carrying out of several determinations at one time. When the temperature of the bath reached 135° C the rack was placed in the bath. Some slight difficulties were occasionally encountered when dissolving the polymer but were eventually dissolved with vigorous shaking. As before, reproducible measurements of the temperature of dissolving could not be obtained. The same precipitation temperatures, within experimental error (±0.2° C), were observed on cooling the same samples of the fractionated polymer. Reproducible results were also obtained when fresh solutions of the unfractionated samples were used. The rate of cooling in these experiments was ca. 0.5 C °/min.

D. Viscosity Measurements

Typical Ubelhode viscometers (calibrated according to ASTM (15) standards to obtain kinetic energy corrections) were used for the viscosity determinations. The values obtained for the calibration constants α^* and β appear in the Appendix. The temperature of the silicone oil bath in which the viscometer was immersed was held constant to ±.05° C during the

viscosity measurements. Calibrated thermometers were used in the oil bath.

Values of η_{sp}/c and $\ln \eta_{rel}/c$ were calculated from the viscosity measurements. These were used to obtain the intrinsic viscosity. A double extrapolation of these values to zero concentration was used in drawing the plots, where the lines meet at a common intercept to give the intrinsic viscosity, $[\eta]$. These two lines were drawn to a best fit and the k' and k" values of the Huggins viscosity relationship (40) were calculated from the slopes and the intercepts. In all the plots the difference in k' and k" equaled 0.50 $\pm$0.03. An example appears in the figures 7 and 8 from the present investigation.

For each intrinsic viscosity determination solutions of several concentrations were prepared for each fraction (three for α-chloronaphthalene and four for diphenyl ether). These solutions were prepared individually rather than by using the dilution technique. Weighed samples were added into a volumetric flask which was immersed in the thermostat at the temperature at which the measurement was to be carried out and solvent added to the volumetric flask mark. The manner in which the effect of the change in density with temperature of the solvent was accounted for will be shown

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(40) P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953, p. 310.

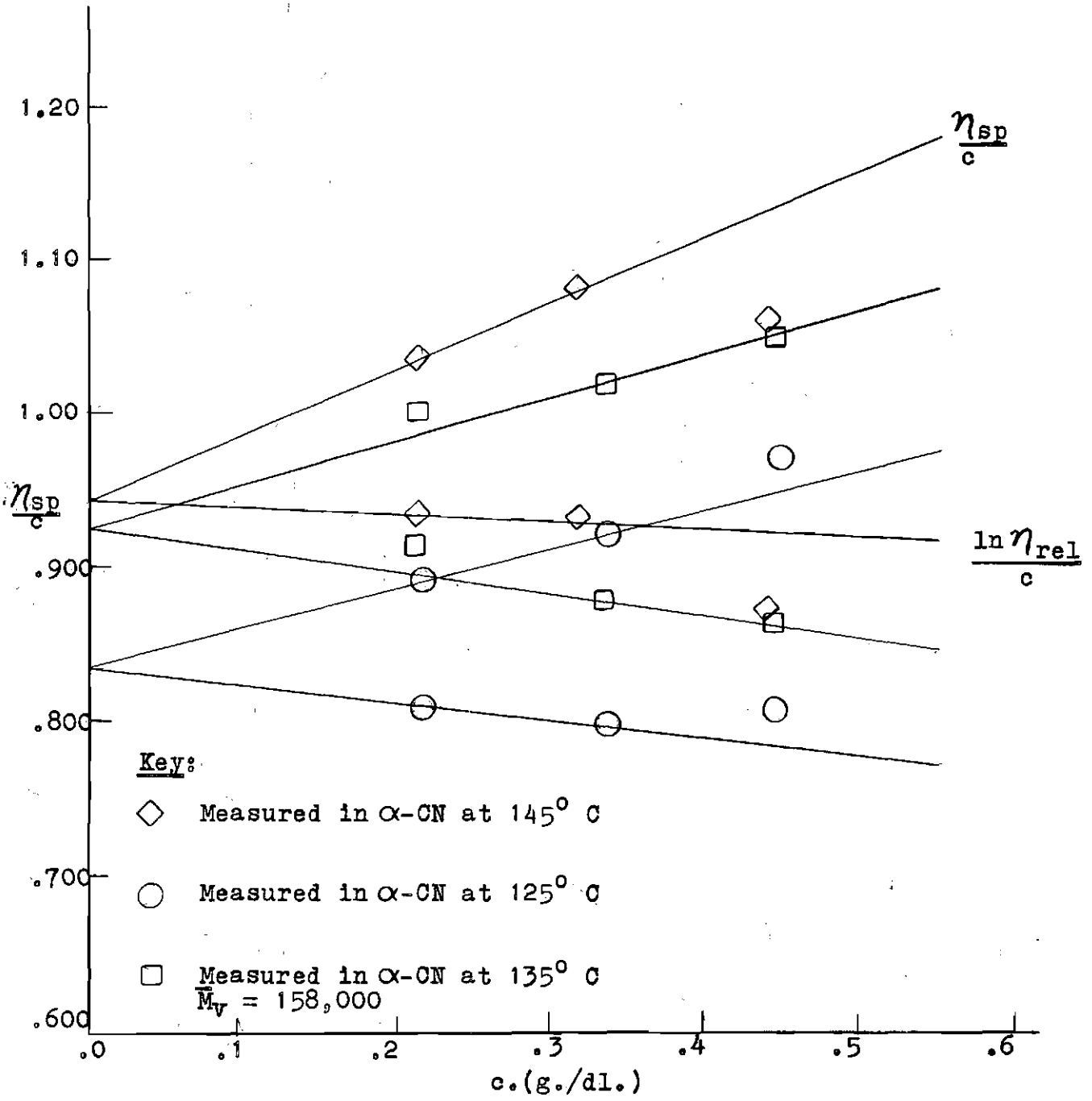

Figure 6. Intrinsic Viscosity Data in α-Chloronaphthalene

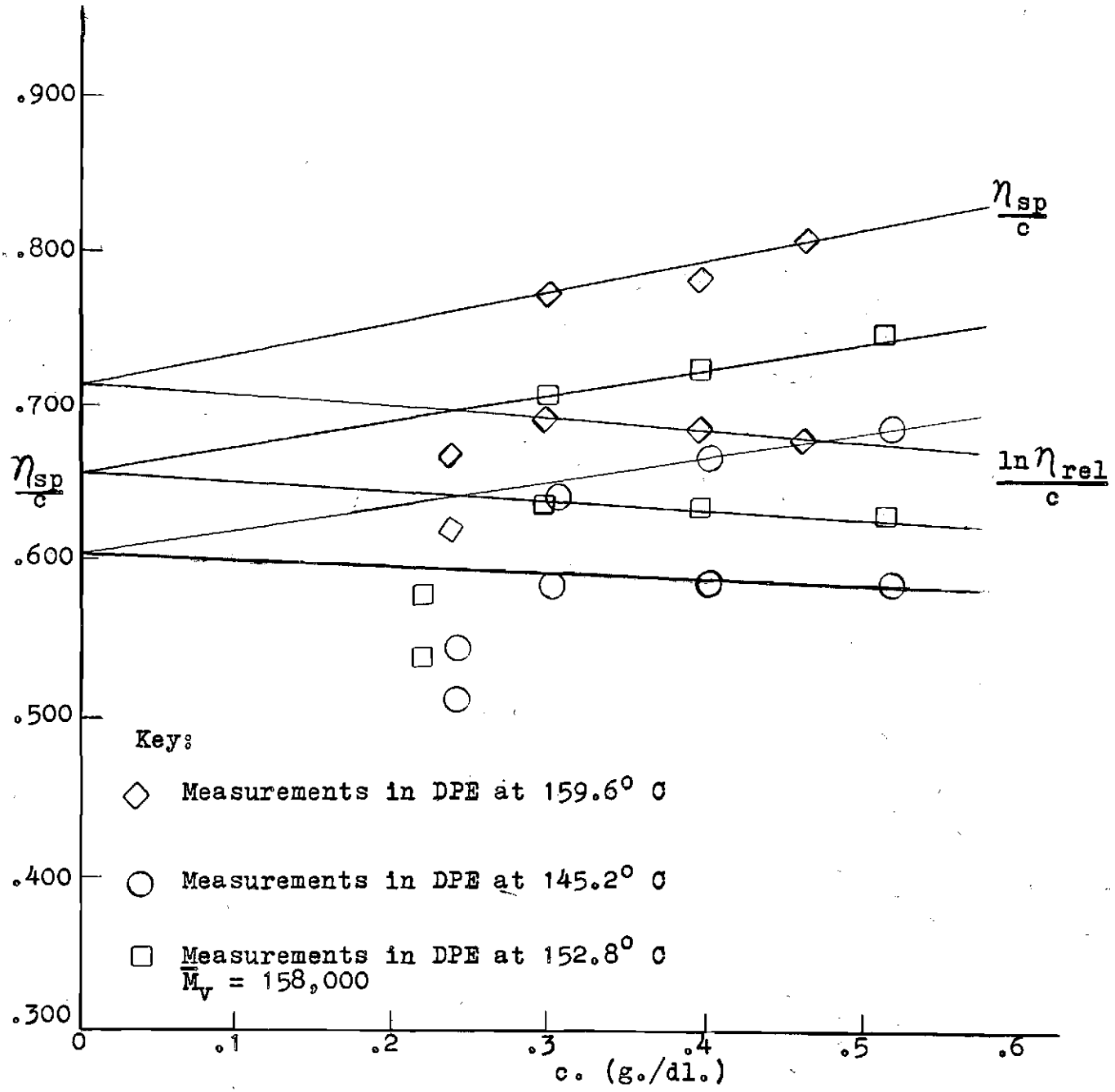

Figure 7. Intrinsic Viscosity Data in Diphenyl Ether

later. The temperature dependence of the density for a solvent was either obtained directly from literature values (27, 41) or else was calculated from them by extrapolation.

The polymer solutions were filtered through a coarse sintered glass frit filter (clogging occurred with a fine frit). The filter was heated by nichrome wire which was wrapped around the filter and then covered with absestos. Preliminary tests with the filter were made until a setting on the variac was found which prevented precipitation of the polymer. The filter and the viscometer were washed with hot solvents and then dried after each solution was investigated. Unfiltered liquids were never put directly into the viscometer in order to prevent clogging of the capillary. All solutions were filtered directly into the viscometer. Suction was used to draw the solution up through the capillary. The flow time was measured with a Meylan stopwatch which could be read to $\pm$0.05 seconds. Efflux times were taken for each concentration until three or more agreed to within $\pm$0.05 seconds. After the flow time was measured for each concentration at the three temperatures the viscometer was throughly rinsed three times with decalin and once with xylene.

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(41) D. Moore, L. Burhardt and W. McEwan, J. Chem. Phys., 25, 1235 (1956).

A special piece of apparatus was made so that the viscometer would not have to be handled at high temperatures during the cleaning process. The diagram below shows the essential features.

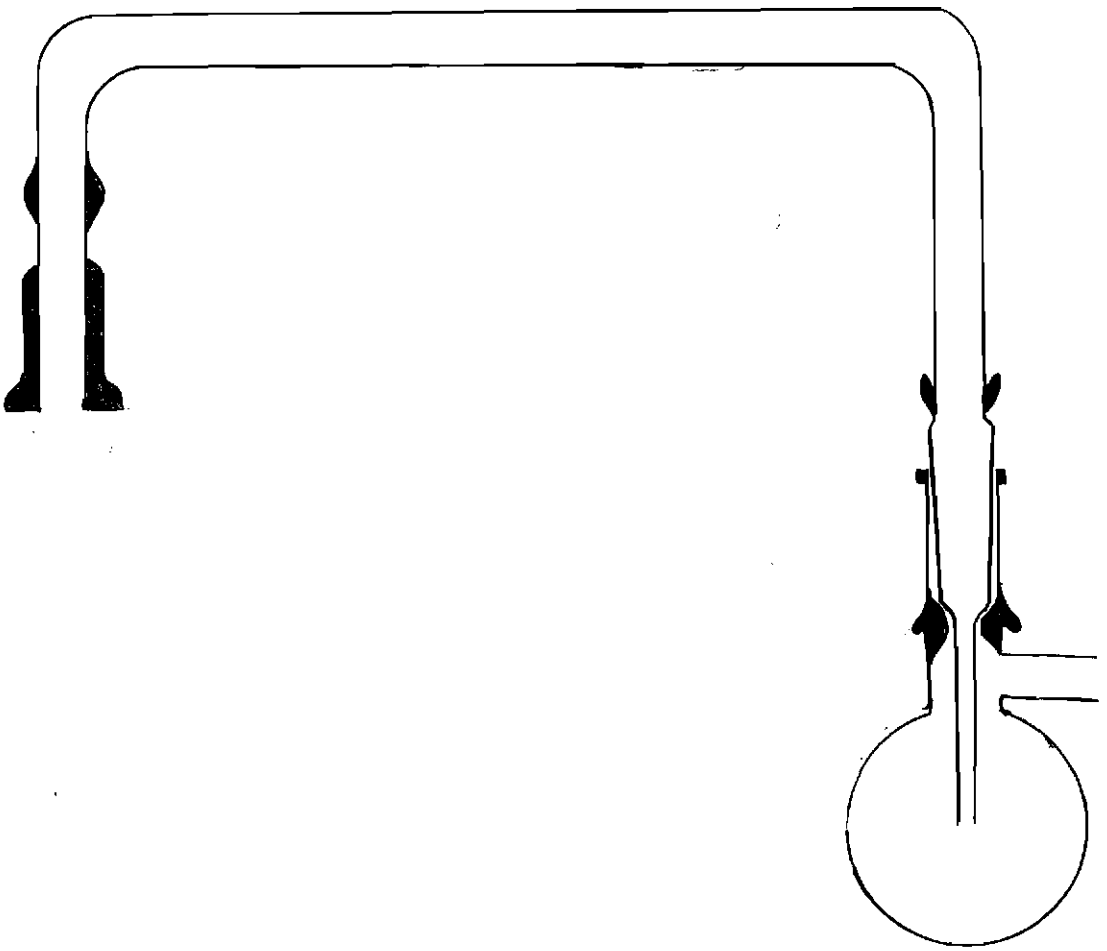

Figure 8. Device for Cleaning Viscometer

A is a ground glass joint (10/30) that fits directly on top of the viscometer, which is immersed in the oil bath. Flask B extends outside of the bath so that as the cleaning solution accumulates in flask B it is removed without the necessity of touching the viscometer.

Viscosity data were taken over a range of concentration and temperatures using two main solvents, α-chloronaphthalene and diphenyl ether. The data appear in the Appendix. Degradation of the polymer at these temperatures was minimized by making up the solutions to be 0.3 per cent in Ionol and 0.05 per cent in stannous sterate. When the viscosity of each solution was measured as a function of temperature the following procedure was followed: the flow time was measured in one oil bath at one temperature, then in a second oil bath at a different temperature. Meanwhile, the first bath was changed to a third temperature and the flow time was then measured in it. In this manner three flow times at three different temperatures could be measured in a reasonable length of time giving three intrinsic viscosities even though there was not sufficient silicone oil available to permit the operation of three different constant temperature baths.

The concentration of each polymer solution was determined after the flow time measurement by means of dry weight analysis performed as follows: the polymer solution was poured into a previously weighed weighing bottle which was

again weighed when it reached room temperature (in the calculation of the concentration the change in density with temperature was taken into account). The solvent was evaporated in vacuo at a temperature between 60°-80° C and weighed again to determine the weight of the dried polymer.

CHAPTER III

RESULTS AND DISCUSSION

A. Fractionation of the Polymer

The fractionation procedure gave a series of fractions differing in molecular weight. The molecular weights of these fractions were determined by means of viscometry. The intrinsic viscosities of some of the fractions (some of which had to be combined to obtain a quantity sufficient for a measurement) were estimated from the viscosities measured at 135° C in decalin. For each fraction a single measurement was made and a value of $[\eta]$ calculated from the Huggins (42) relations with the usual requirement that $k' - k'' = 0.50$

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c$$

$$\ln \eta_{rel}/c = [\eta] + k''[\eta]^2 c$$

Molecular weights were then calculated from the equation (27) of Kinsinger

$$\log [\eta] = -3.959 + .80 \log \bar{M}_v$$

In Columns 1, 2, and 3 of Table 1 the experimental results of the fractionation are presented. Fraction 270 exhibits a much lower molecular weight than expected. This

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(42) M. L. Huggins, J. Am. Chem. Soc., 64, 2716 (1942).

reversal may be due to the formation of cavities in the column packing. In such a case, the eluting liquid does not extract the polymer in the cavity at the appropriate time and so the unextracted low molecular weight polymer from the cavity comes down later on in the fractionation. This effect has been observed by Kenyon and Salyer (37).

Another possible explanation of the reversal, suggested by new work of Natta's (43) on stereospecific polymers, is that the original polypropylene sample was composed of two "sub-samples" of quite different degree of isotacticity. The "sub-sample" of higher stereoregularity would be expected to exhibit lower solubility. Hence, the low molecular weight fraction 270 could be a more stereoregular sample than the low molecular weight fractions extracted during the initial stages of the fractionation.

In order to characterize a continuous distribution of molecular weights in a polydisperse mixture a differential weight fraction distribution w_x is defined as follows; $w_x dx$ is the weight fraction of chains whose molecular weights lie in the range between x and x + dx. One then defines an intregral weight distribution function W_x as

$$W_x = \int_0^x w_x dx$$

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(43) G. Natta, Makromol. Chem., 35, 93 (1960).

In practice one obtains a series of fractions each of whose average molecular weight is measured and whose weight fractions are labelled w_1, w_2..... . These fractions each contain polymer molecule of molecular weights both greater and less than the average molecular weight x.

In column 4 of Table 1 is the cumulative or integral weight fraction of the first x fractions. The integral weight distribution can be approximately evaluated by assuming each fraction to be monodisperse.. Then

$$W_x = \sum_{j=1}^{x} w_j = \sum_{j=1}^{x} \left(\frac{g_i}{\sum_{j=1}^{n} g_i} \right)$$

where w_j is the weight fraction of polymer molecules in the $_j$th fraction and g_i is the weight of the $_i$th fraction, and n is the total number of fractions.

A more realistic assumption (44) is that the distribution within each fraction is symmetrical about the average molecular weight. This assumption corresponds to half the fraction having molecular weights higher and half lower than the average molecular weight of the fraction. The curve on Figure 9 shows the corresponding values of W_x, the "corrected" cumulative weight fraction through the $_x$th fraction, plotted

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(44) G. V. Schulz and A. Dinglinger, Z. phys. Chem., B43, 47 (1939).

Table 1. Experimental Fractionation Data

	Fraction	Molecular Weights $\bar{M}_v$	g_i Weight (g.)	Cumulative Weight Fraction	Corrected Cumulative Weight Fraction	Temperature of elution T_{el} °C
A	1-24	16,700	.1367	.0064	.0032	100°
B	51-57	20,800	.4255	.0200	.0162	100°
C	71-75	28,000	.8518	.0401	.0363	100°
D	179	42,000	2.6623	.1223	.1154	110°
E	270	48,200	5.1465	.2425	.2375	120°
F	203-4	79,000	8.7659	.4130	.4077	110°
G	243-4	229,000	10.7169	.5049	.4984	120°
H	353-63	254,000	20.7978	.9748	.9692	158°

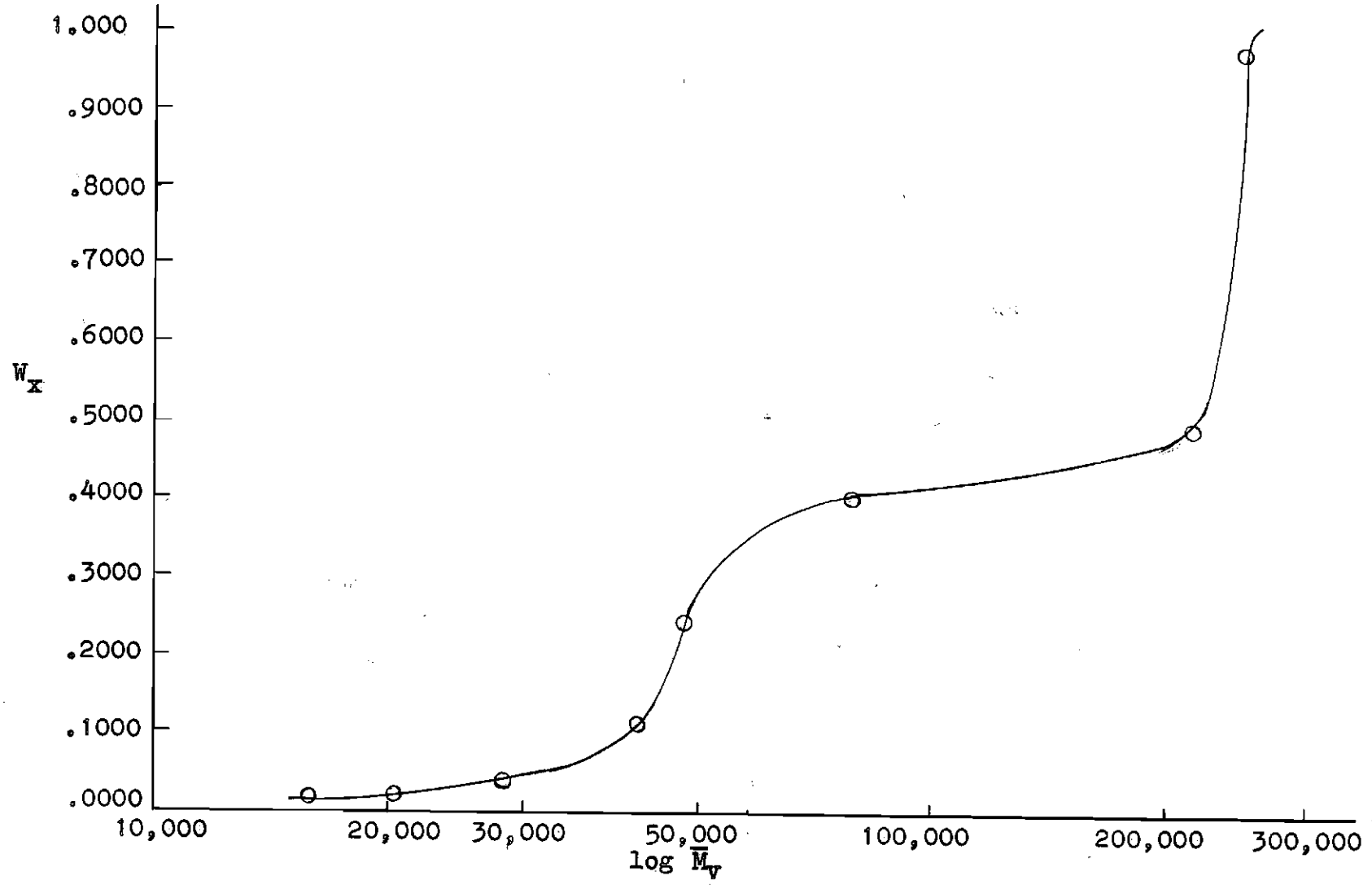

Figure 9. Plot of W_x vs. log $\overline{M}_v$ for the Fractions Collected from the Column

against log M_x where W_x is evaluated as follows: if w_j is the weight fraction of the $_j$th fraction, then:

$$W_x = \sum_{j=1}^{x-1} w_j + \frac{w_x}{2} = \sum_{j=1}^{x-1} \frac{g_i}{\sum_{i=1}^{n} g_i} + 2\frac{g_i}{\sum_{i=1}^{n} g_i}$$

where the additional assumption is made that only adjacent fractions overlap.

The integral weight distribution curve would appear to indicate that reasonable fractionation has taken place in the low molecular weight range (i.e. below 200,000). The results in the high molecular weight range appear less encouraging. In either case, however, measurements of both weight and number averages of the fractions should be made before definitive statements about the sharpness of the fractions can be made.

During the fractionation the temperature of the column was increased after collecting the first 171 fractions. The water in the column jacket which maintained a temperature of 100° C was replaced by toluene; this changed the temperature of the column to 110° C. The reason for the increase in the temperature at this point was that no more visible precipitation of the polymer occurred at 100° C after fraction 170 was collected. The column was kept at this temperature until the 233rd fraction was collected. From fraction 234 to 304 the temperature of the column was kept at 120° C using acetic

acid in the boiler. The final fractions were collected at a temperature of 158° C, using ethyl carbonate in the boiler. The various conditions are summarized in Table 2.

Preliminary experiments were carried out on the solubility of polypropylene at various temperatures to determine the most appropriate fractionation temperature. The initial temperature determined was apparently too low for eluting all of the polymer because of adsorption of polypropylene on the celite. In order to desorb the polymer additional thermal energy was therefore required to desorb the polymer. It may be concluded that the best elution temperature for a fraction is not determined solely by its solubility behavior.

The column technique would appear to be a very convenient method for studying the molecular weight distributions in polymer samples.

Table 2. Conditions of Fractionation

Fractions	Solvent(s)	Temperature	Total weight of polymer collected
1-170	decalin, diethylene gylcol diethylether	100° C	1.47 g.
171-233	decalin	110° C	7.65 g.
234-304	decalin	120° C	10.46 g.
305-400	decalin	158° C	1.64 g.
	TOTAL		21.22 g.

B. Phase Equilibria

Closer examination of the phase diagram for polypropylene-naphthalene excluded the possibility for liquid-liquid separation in the concentration range measured. The monotonic curves in Figure 10 indicate crystal-liquid separation for the system (45); they represent the temperature at which there is a change from a single liquid phase into a two phase system liquid (amorphous) + solid (crystalline). Table 3 contains the data which is plotted in Figure 10. The plots of precipitation temperature vs. composition may also be viewed as plots of solubility vs. temperature. (Since a polymer sample consists of series of homologous species its mixtures with a solvent should be looked at as polycomponent systems). One would expect that the highest molecular weight species should have the lowest solubility but this is not borne out by the data in Figure 10.

It was found by Richards (46) that polyethylene samples of the same average molecular weight but of different breadth of distribution have different solubilities in a given solvent; in particular, a fraction having a broad molecular weight distribution exhibited higher solubility than do fractions of narrow distribution. In view of this, the distribution of the polymer of molecular weight 261,000

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(45) Flory, op. cit., pp. 571-576.

(46) R. B. Richards, Trans. Faraday Soc., 42, 10 (1946).

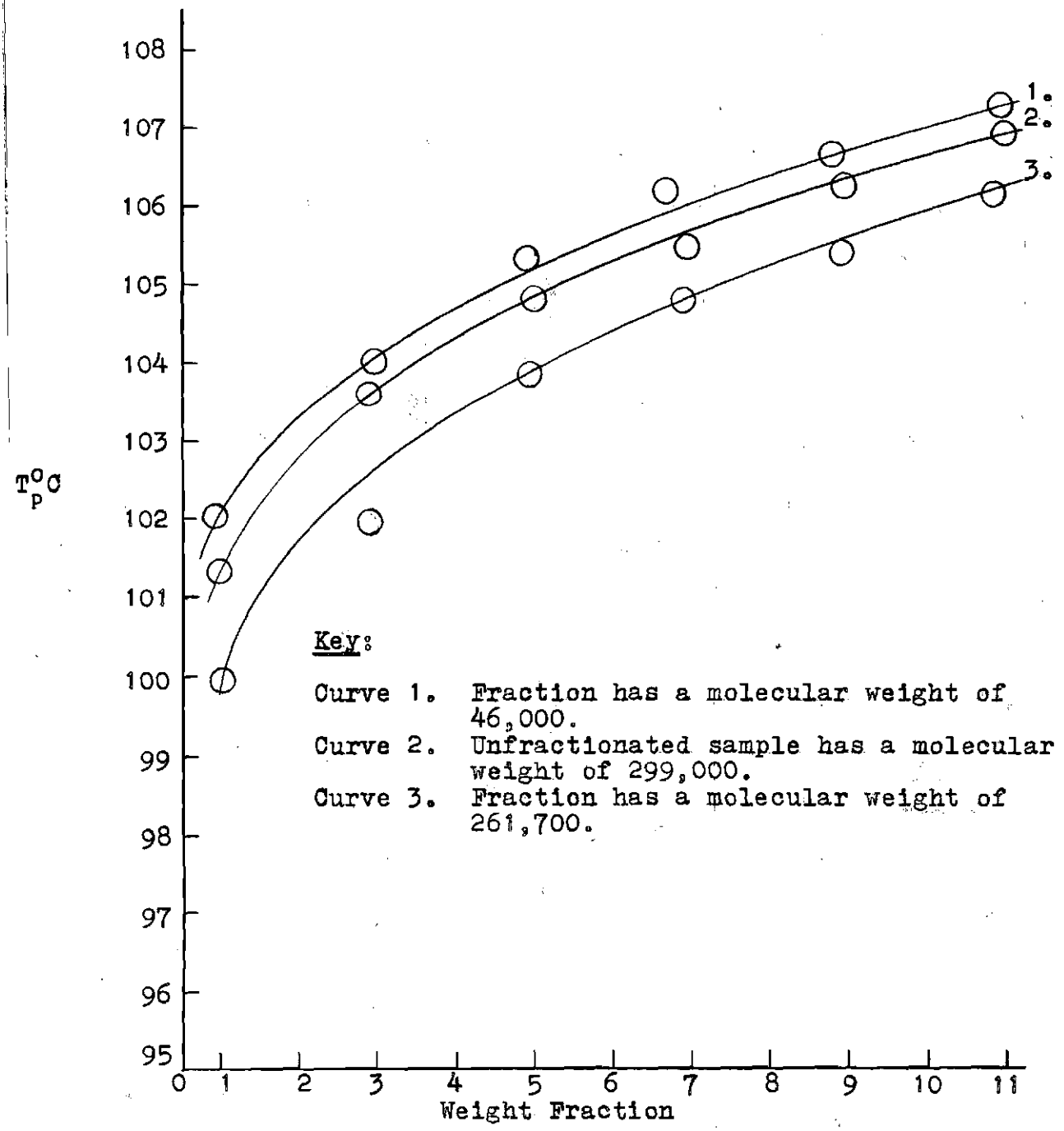

Figure 10. Phase Diagram for Naphthalene-Polypropylene System

Table 3. Precipitation Temperatures of Polypropylene in Naphthalene

A. Unfractionated Polymer of M. W. 299,000 (Curve 2)							
Weight Fraction of Polypropylene	1.04	2.95	5.03	6.97	8.99	11.00	29.99
Precipitation Temperature, T_p °C	101.3	103.5	104.8	105.4	106.2	106.9	115.5
B. Polymer fraction of M. W. 261,700 (Curve 3)							
Weight Fraction of Polypropylene	1.03	2.95	4.95	6.92	8.97	10.83	
Precipitation Temperature, T_p °C	100.0	101.9	103.9	104.8	105.3	106.1	
C. Polymer fraction of M. W. 46,800 (Curve 1)							
Weight Fraction of Polypropylene	.97	3.02	4.90	6.71	8.79	10.92	
Precipitation Temperature, T_p °C	102.0	104.0	105.4	106.2	106.6	107.2	

may be due to degradation actually broader than that of the unfractionated sample. This is so in view of the prolonged exposure to high temperatures during the fractionation procedure.

According to the presently accepted theory of crystallization of polymers, the process of crystallization involves the two basic steps of nucleation and growth. Before nucleation can occur a critical size of a growing crystalline embryo must be attained and only below the precipitation temperature does this occur (47). Consider the change of free energy occurring when a spherical crystalline body of radius r is formed from the liquid phase:

$$\Delta F = (\mu_c - \mu_1)\, n' + 4\pi r^2 \sigma$$

where μ_c and μ_1 are the free energies per molecule in the bulk crystal and bulk liquid, respectively. The number of molecules in the sphere is given by n', and σ is the interfacial free energy per unit area.

Since $n' = \frac{4}{3}\frac{\pi}{v} r^3$ where v is the volume per polymer molecule, we have

$$\Delta F = (\mu_c - \mu_1)\, \frac{4}{3}\frac{\pi}{v} r^3 + 4\pi r^2 \sigma$$

The figure below shows the value of the free energy of formation of a crystalline embryo from the liquid for

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(47) L. Mandelkern, "Crystallization Kinetics in Polymeric Systems" in Growth and Perfection of Crystals, Edited by R. H. Doremus, B. W. Roberts, D. Turnbull, New York, N. Y., John Wiley and Sons, Inc., 1958, p. 477.

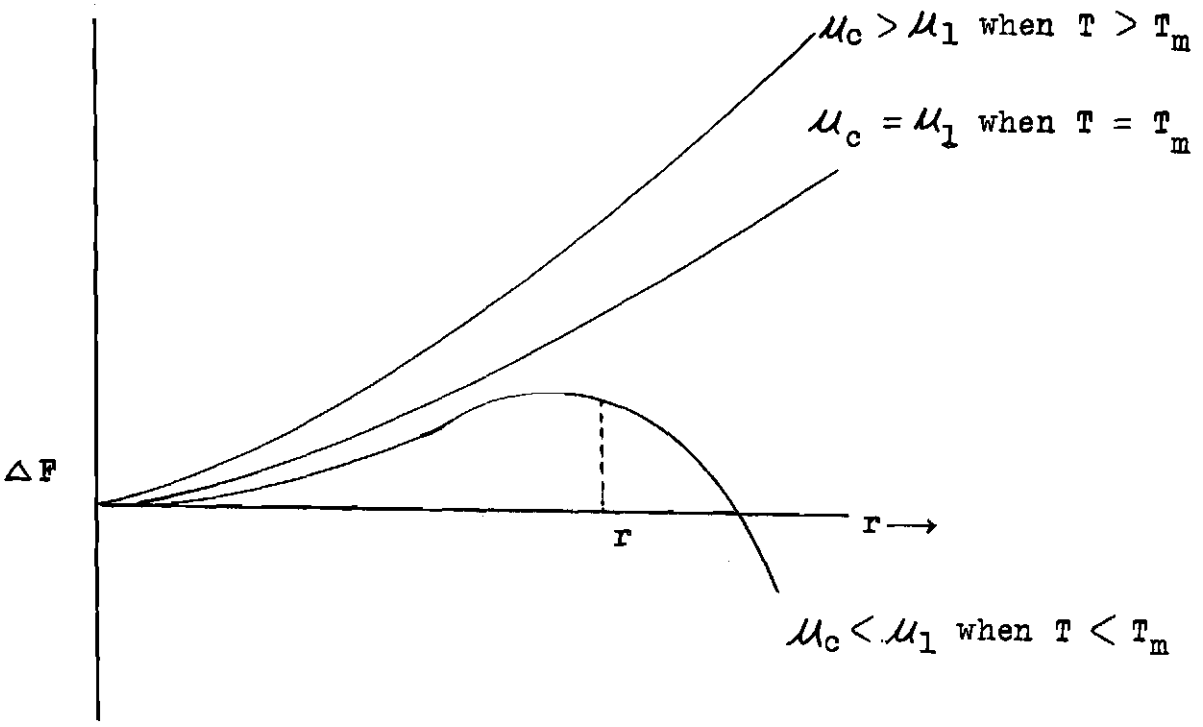

Figure 11. Dependence of ΔF on the Size of the Spherical Radius

the three cases indicated (where T_m represents the melting point of the polymer-diluent mixture).

It can be seen from the curves that only at temperatures below the equilibrim melting point can nucleation be a spontaneous process ($\frac{\partial F}{\partial r} < 0$). The nucleation rate increases with an increase in supercooling (that is, the greater the difference between $T - T_m$). The reason for this is that at lower temperatures the "critical size" of the nucleus, i.e., the value of r above which $\frac{\partial F}{\partial r}$ is negative, becomes smaller.

Further growth of a nucleus can be considered to take place by diffusion of the polymer up to the growing crystal

followed by proper orientation of the molecule so that it can crystallize. If diffusion is the rate determining step in the growth process (as it might be expected to be in very dilute solutions) one would then expect higher molecular weight fractions to grow slower. Hence, a high molecular weight fraction might be expected to have a lower precipitation temperature in the dilute solution range than a low molecular weight fraction even though the reverse were true at higher concentrations where diffusion was no longer the rate determining step. No such cross-over is indicated in Figure 10 but neither is it excluded, due to the restricted concentration range investigated.

C. Viscosity Measurements

The influences of temperature and solvent on the intrinsic viscosity of polypropylene are reflected in the data shown in Table 4 (where the units of $[\eta]$ are dl/g.).

The results which are shown in graphs 13 & 14, are consistent with known results for other vinyl type polymers (48); a change in temperature in a "poor" solvent causes a larger increase in the intrinsic viscosity than in a good solvent. This may be ascribed to the increase in the number of contacts between polymer segments and solvent molecules described previously. The positive temperature coefficients

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(48) Flory, op. cit., pp. 611-626.

Table 4. Intrinsic Viscosity Data for Polypropylene

A. In α-chloronaphthalene

Molecular weight	$[\eta]_{125°C}$	$[\eta]_{135°C}$	$[\eta]_{145°C}$	$\frac{d \ln[\eta]_{135°C}}{dt} \times 10^2$
158,000	.835	.925	.945	.22
242,000	1.10	1.18	1.20	.12
278,600	1.21	1.24	1.26	.08
316,600	1.31	1.40	1.41	.09
1,026,000	2.95	3.10	3.10	.15

B. In Diphenyl Ether

Molecular weight	$[\eta]_{143.2°C}$	$[\eta]_{152.8°C}$	159.6 C	$\frac{d \ln[\eta]}{dt} \times 10^2$
158,000	.605[a]	.660	.715	1.7
242,000	.775	.870	.940	2.3
278,000	.775	.915[b]	.960	2.6
316,600	.915	1.05	1.15	2.6
1,026,000	1,70	1.84	2.00	4.1

[a]Measured at 145.2 C°

[b]Measured at 153.2 C°

observed are in contrast with those of cellulose derivatives (49) which exhibit negative temperature coefficients. Since these negative coefficients are thought to be due to a rapid

(49) P. J. Flory, O. K. Spurr, Jr. and D. K. Carpenter, J. Polymer Sci., 27, 231 (1958).

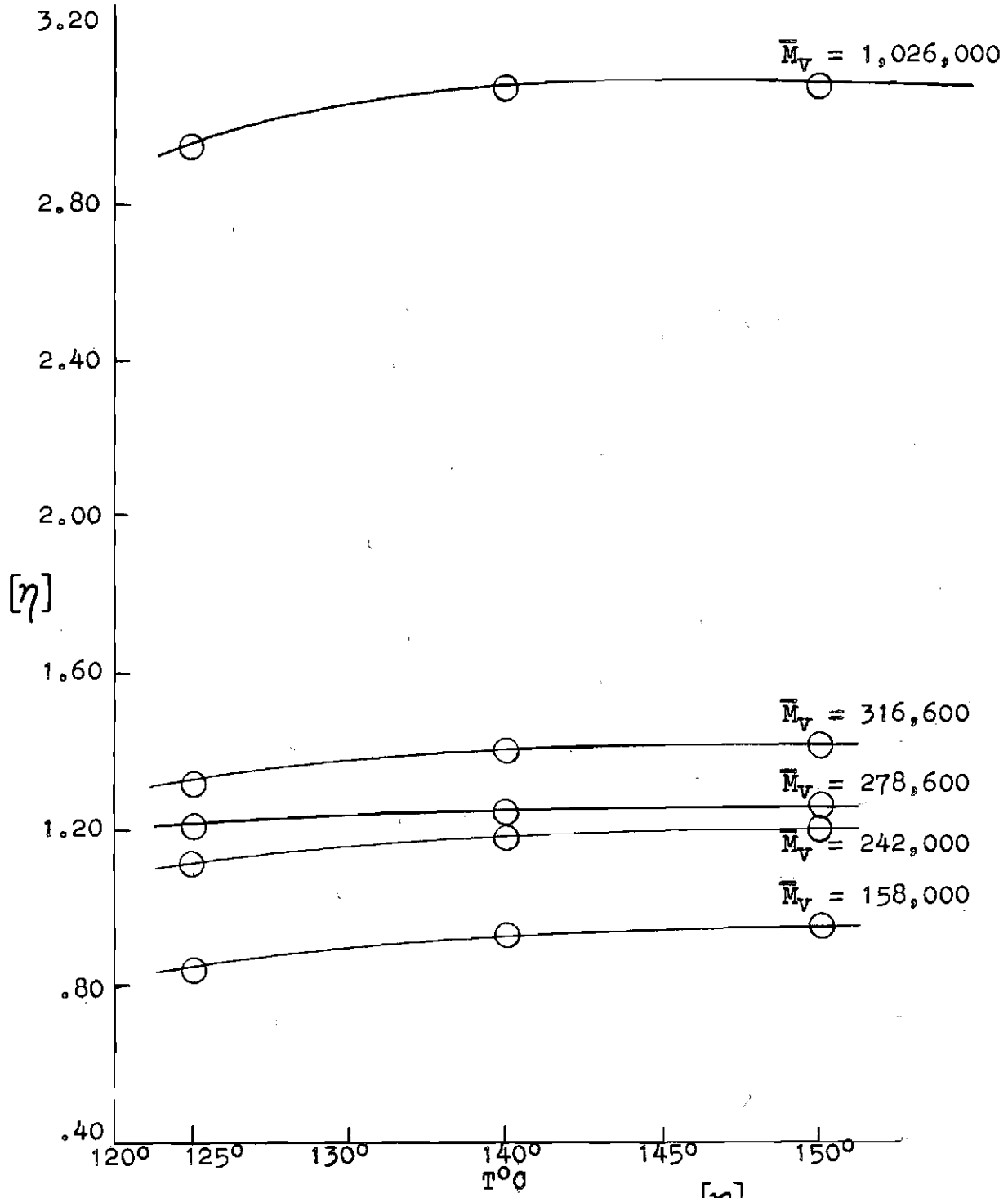

Figure 12. Temperature Dependence of $[\eta]$ in α-Chloronaphthalene

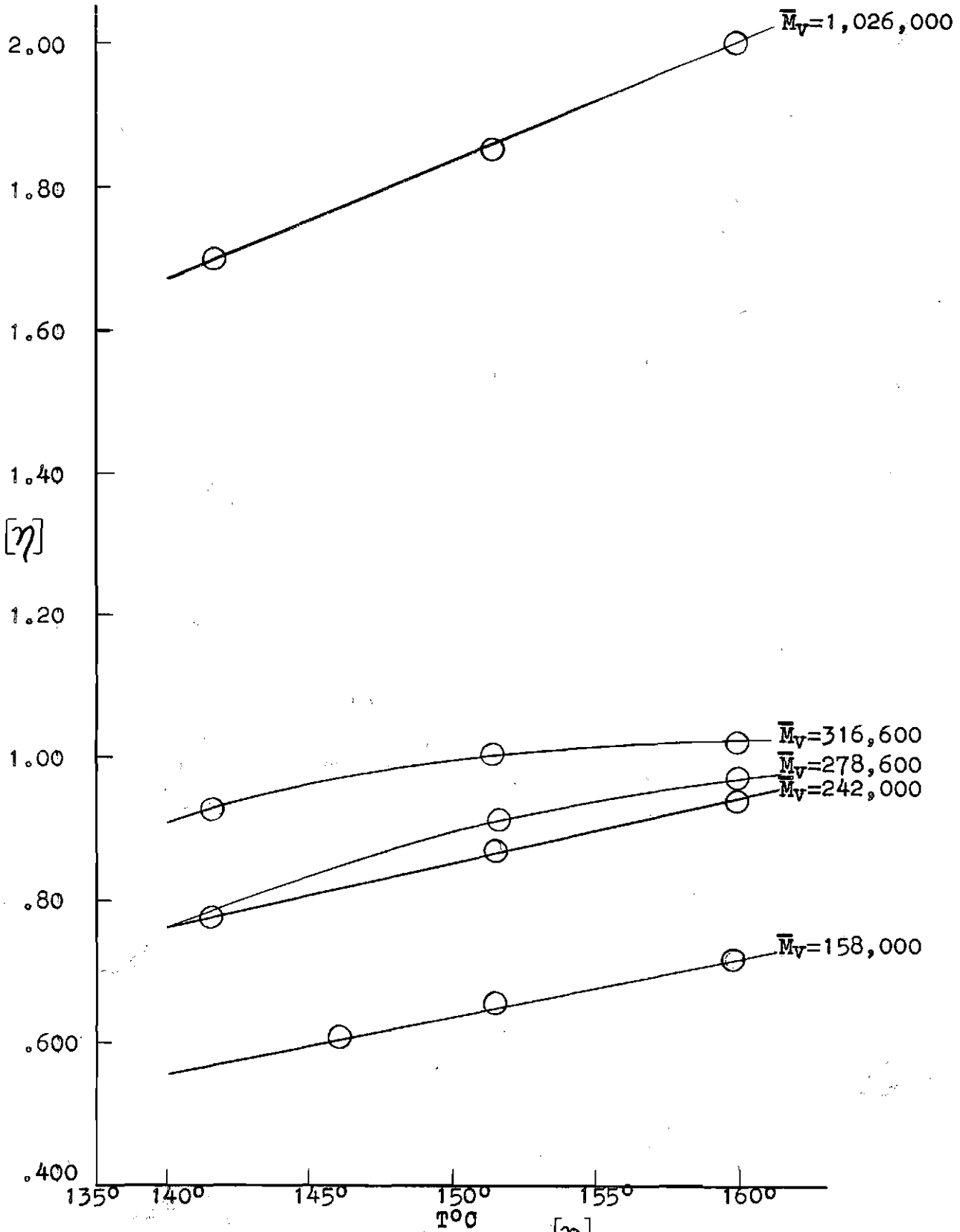

Figure 13. Temperature dependence of $[\eta]$ in Diphenyl Ether

decrease in $\overline{R_0^2}/M$ with temperature as restrictions to internal rotations are overcome, there is apparently no abnormally large "stiffness" present in polypropylene molecules.

This conclusion has been tested by performing certain numerical calculations. Using only the data of other workers, the unperturbed value of $\overline{R_0^2}/M$ for the polypropylene molecule was estimated as follows using a modification of the Orofino and Flory relationship, equation (3):

$$2.76 \times 10^{-24} \overline{A_2}\ \overline{M_w}\ \Phi\ [\eta]^{-1} = \overline{F(X)}(\alpha^2 - 1)$$

(where the quantities have been defined in the introduction). From measurements of $[\eta]$, $\overline{A_2}$ and $\overline{M_w}$ in a good solvent, α is calculated, and from α and $[\eta]$, $[\eta]_\theta$ is obtained from equation (2). The values of $\overline{M_w}$, $\overline{A_2}$ and $[\eta]$ for polypropylene in α-chloronaphthalene at 125° C of Kinsinger (27) and at 145° C of Parrini, Sebastiano and Messina (50) were used to calculate intrinsic viscosities of polypropylene at the theta condition in this way. A standard plot of $(\alpha^2-1)\ F(X)$ against α^2-1 was first made so that α^2 could be determined through use of equation (3). In this connection Φ was taken to be equal to 2.4×10^{21}. Since in equation (1),

$$[\eta]_\theta = \Phi \left(\frac{\overline{R_0^2}}{M}\right)^{3/2} M^{\frac{1}{2}}$$

a plot of $[\eta]_\theta$ versus the square root of the molecular weight results in a value for $(\overline{R_0^2}/M)$. Figure 15 shows the points

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(50) P. Parrini, F. Sebastiano and G. Messina, Makromol. Chem., 38, 27 (1960).

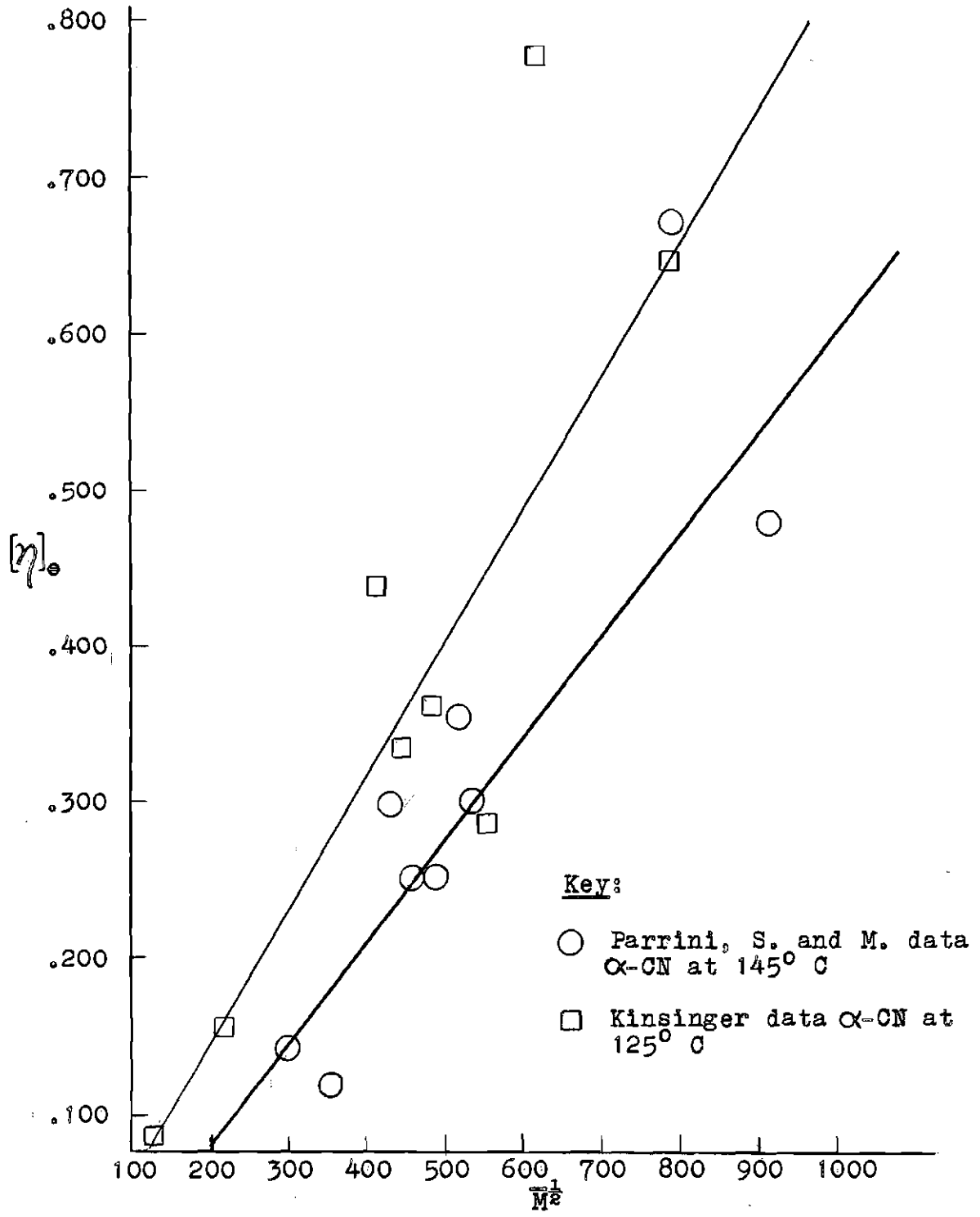

Figure 14. Values of $[\eta]_\Theta$ vs. $\overline{M}^{\frac{1}{2}}$ for Polypropylene

Two such values from their data were calculated and shown in Table 5.

Table 5. Estimates of the Ratio $\overline{R_o^2}/M$ (cm.^{2}/g./mole) in α-chloronaphthalene

Temperature °C	145°	125°	30° [a]
$\overline{R_o^2}/M \times 10^{-16}$	.45	.52	.79

[a] extrapolated value

As explained in the introduction, this ratio depends on the bond dimensions and valence angles, and on hindrance to rotation as well as the molecular weight per repeating unit. For comparison with isotactic polystyrene (51) and polyisobutylene (52) the value of the mean-square end-to-end distance per repeating unit $\overline{R_o^2}/n$ (equal to $M_o \times \overline{R_o^2}/M$) for these polymers were calculated to be 58×10^{-16} cm.^{2} (at 30°) and 33×10^{-16} cm.^{2} (at 30°), while the value calculated for isotactic polypropylene, 31×10^{-16} cm.^{2} (at 30°), is seen to be in the same range. This confirms the conclusion made in the previous paragraph, that polypropylene exhibits a stiffness similar to other vinyl polymers.

A change in temperature affects the intrinsic viscosity through changes in both $\overline{R_o^2}/M$ and α^3 as can be seen from the

(51) W. R. Krigbaum, D. K. Carpenter and S. Newman, J. Phy. Chem., 62, 1586 (1958).

(52) Flory, op. cit., p. 618.

Flory-Fox equation (1),

$$[\eta] = \Phi (\overline{R_0^2}/M)^{3/2} M^{\frac{1}{2}} \alpha^3$$

Therefore,

$$\frac{d\ln[\eta]}{dt} = \frac{d\ln(\overline{R_0^2}/M)^{3/2}}{dt} + \frac{d\ln\alpha^3}{dt}$$

Estimates of the magnitude of the two terms responsible for the temperature coefficient of the intrinsic viscosity can be made as described above. As seen in Table 5 the data of Kinsinger and Parrini, Sebastiano and Messina indicate that $\overline{R_0^2}/M$ decreases with increasing temperature. The temperature coefficient of $(\overline{R_0^2}/M)$ for isotactic polypropylene is $-.35 \times 10^{-18}$ cm.^{2}/g./mole/deg. which compares favorably with the value for atactic polystyrene $-.65 \times 10^{-18}$ cm.^{2}/g./mole/deg. (53). The estimate of α values from equation (3) as described above in calculating $[\eta]_\theta$ when combined with the values measured in α-chloronaphthalene in this work yield the results in Table 6.

Table 6. Estimates of the Expansion Factor, α, in α-chloronaphthalene at 135° C and 145° C

Molecular weight	$[\eta]_{135°}$	$[\eta]_{145°}$	$[\eta]_{\theta=135°}$	$[\eta]_{\theta=145°}$	$\alpha_{135°}$	$\alpha_{145°}$
158,000	.915	.945	.262	.230	1.52	1.60
242,000	1.18	1.20	.342	.303	1.51	1.58
278,600	1.24	1.26	.369	.328	1.50	1.57
316,600	1.40	1.41	.399	.354	1.52	1.59
1,026,000	3.10	3.10	.768	.688	1.59	1.65

(53) Flory, op. cit., p. 615 and p. 618.

This data shows the expected temperature dependence of the expansion factor α, which is to increase with temperature when above the theta temperature, which is the case for polypropylene in α-chloronaphthalene. However, an unexplained anomaly is the fact that both the data reported in this thesis and the data of Kinsinger and Parrini, Sebastiano and Messina yield α values that do not increase with M at constant temperature. Theory predicts, and is adequately borne out by experiment (48) that if the molecular weight exponent in the equation

$$[\eta] = K M^a$$

relationship is greater than 0.5, as is the case here, the intramolecular expansion factor should <u>increase</u> with molecular weight. The results in Table 6 do not follow this trend. They are essentially constant with respect to molecular weight. The same conclusion is obtained from the data of this thesis using the relationship

$$\frac{[\eta]_{CN\ 145^oC}}{[\eta]_{DPE\ 143.2^oC}} = \frac{\alpha^3_{CN}}{\alpha^3_{DPE}} = \alpha^3_{CN}$$

where the second form of writing arises from the circumstance that 143.2° C is very near the theta temperature for diphenyl ether (θ = 145.2° C) (at the theta temperature (θ) theory predicts α must equal unity irrespective of molecular weight). The values of α calculated in this manner are presented in Table 7.

Table 7. Approximate Values of α from Measurements of Intrinsic Viscosities in Diphenyl Ether and α-Chloronaphthalene

Molecular weight	$[\eta]_{DPE, 143.2^\circ C}$	$[\eta]_{CN, 145^\circ C}$	α^3_{CN}	α_{CN}
158,000	.605[a]	.915	1.56	1.16
242,000	.775	1.20	1.55	1.15
278,600	.775	1.26	1.63	1.18
316,600	.915	1.41	1.52	1.15
1,026,000	1.70	3.10	1.82	1.22

[a]Measured at 145.2° C

Again we find the anomaly that α is essentially molecular weight independent. The reason for this is not apparent.

To conclude, the results of this preliminary study of the configuration of isotactic polypropylene indicate that no significant difference exists between it and other vinyl type polymers.

APPENDIX

A. Viscosity Data in α-chloronaphthalene

$\bar{M}_v$	T°C	c(g./dl.)	η_{rel}
158,000	125°	0.215	1.191_5
	125°	0.335	1.308_5
	125°	0.447	1.434_5
	135°	0.214	1.215
	135°	0.331	1.338
	135°	0.444	1.468
	145°	0.213	1.220
	145°	0.316	1.342
	145°	0.441	1.468
242,000	125°	0.240	1.283_5
	125°	0.363	1.450
	125°	0.444	1.615
	135°	0.238	1.310
	135°	0.361	1.496
	135°	0.442	1.654
	145°	0.236	1.312
	145°	0.357	1.499
	145°	0.438	1.668
278,600	125°	0.246	1.285
	125°	0.331	1.453
	125°	0.438	1.652

A. Viscosity Data in α-chloronaphthalene (continued)

$\overline{M}_v$	T°C	c(g./dl.)	η_{rel}
278,600	135°	0.244	1.316
	135°	0.329	1.487
	135°	0.435	1.696_5
	145°	0.242	1.343
	145°	0.326	1.547
	145°	0.431	1.707
316,600	125°	0.243	1.328
	125°	0.351	1.529_5
	125°	0.450	1.771
	135°	0.242	1.360
	135°	0.348	1.561
	135°	0.447	1.816
	145°	0.241	1.368_5
	145°	0.345	1.578
	145°	0.443	1.837
1,026,000	125°	0.238	1.741
	125°	0.346	2.417
	125°	0.506	3.655
	135°	0.236	1.847
	135°	0.344	2.492
	135°	0.502	3.691
	145°	0.234	1.869
	145°	0.341	2.530
	145°	0.498	3.786_5

B. Viscosity Data in Diphenyl Ether

$\bar{M}_v$	T°C	c(g./dl.)	η_{rel}
158,000	145.2°	0.242	1.132
	145.2°	0.303	1.195
	145.2°	0.402	1.267
	145.2°	0.520	1.357
	152.8°	0.240	1.138
	152.8°	0.310	1.212
	152.8°	0.399	1.289
	152.8°	0.517	1.385_5
	159.6°	0.238	1.158
	159.6°	0.299	1.230
	159.6°	0.396	1.309
	159.6°	0.513	1.414
242,000	143.2°	0.319	1.235
	143.2°	0.390	1.338
	143.2°	0.535	1.505
	153.2°	0.316	1.268
	153.2°	0.386	1.410
	153.2°	0.556	1.590
	159.6°	0.308	1.283
	159.6°	0.376	1.422
	159.6°	0.516	1.620
278,600	143.2°	0.288	1.235
	143.2°	0.350	1.298

B. Viscosity Data in Diphenyl Ether (continued)

$\bar{M}_v$	T°C	c(g./dl.)	η_{rel}
278,600	143.2°	0.523	1.511
	143.2°	0.621	1.638
	152.8°	0.286	1.266
	152.8°	0.348	1.336
	152.8°	0.519	1.582
	152.8°	0.613	1.719
	159.6°	0.284	1.293
	159.6°	0.345	1.371
	159.6°	0.516	1.640
	159.6°	0.613	1.779
316,600	143.2°	0.211	1.190
	143.2°	0.301	1.307
	143.2°	0.403	1.434
	143.2°	0.517	1.590
	152.8°	0.209	1.220
	152.8°	0.299	1.357
	152.8°	0.400	1.502
	152.8°	0.512	1.681
	159.6	0.207	1.244
	159.6°	0.297	1.388
	159.6°	0.397	1.550
	159.6°	0.509	1.742
1,026,000	143.2°	0.218	1.374_5

B. Viscosity Data in Diphenyl Ether (continued)

$\bar{M}_v$	T°C	c(g./dl.)	η_{rel}
1,026,000	143.2°	0.397	1.846
	143.2°	0.399	1.931
	143.2°	0.592	2.958_5
	152.8°	0.216	1.468
	152.8°	0.393	2.033
	152.8°	0.396	3.134
	152.8°	0.587	3.288
	159.6°	0.215	1.530
	159.6°	0.390	2.154
	159.6°	0.393	2.258
	159.6	0.583	3.493

Calibrations constants for the viscometers;

#1 α^* = .01295 β = 2.412

#2 α^* = .009173 β = .7177

#3 α^* = .0049 β = 1.210

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BIOGRAPHICAL SKETCH

The author was born on April 19, 1937 in the Bronx, New York. He attended local public schools and in June, 1954 was graduated from Evander Childs High School. He attended New York University, (University Heights) where he received a B.A. degree with a major in chemistry. In 1958 he entered the Graduate School of Chemistry of Georgia Institute of Technology where he became a candidate for the degree of Master of Science in Chemistry. He has accepted a position with American Cyanamid Company, at Stanford, Connecticut.

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